

January 1986

NASA-TP-2532 19860011115

Growth of High-Quality Thin-Film Ge Single Crystals by Plasma- Enhanced Chemical Vapor Deposition

R. A. Outlaw and
P. Hopson, Jr.

RECEIVED 1986
JAN 21 1986

LANGLEY RESEARCH CENTER
LIBRARY, STAG
HAMPTON, VIRGINIA

1986

Growth of High-Quality Thin-Film Ge Single Crystals by Plasma- Enhanced Chemical Vapor Deposition

R. A. Outlaw and
P. Hopson, Jr.

*Langley Research Center
Hampton, Virginia*



National Aeronautics
and Space Administration

Scientific and Technical
Information Branch

Summary

Thin-film Ge single crystals ($\approx 10\text{ }\mu\text{m}$) have been epitaxially grown on polished NaCl(100) substrates at 450°C by using plasma-enhanced chemical vapor deposition. Films approximately 1 cm^2 and larger were separated from NaCl by either melting the salt or by differential shear stress upon cooling to room temperature. The ordered growth of the Ge was found to be most sensitive to the initial plasma power and to the continuum flow dynamics within the carbon susceptor. The films were visually specular and exhibited a high degree of crystalline order when examined by X-ray diffraction. The films were found to be p-type with a carrier concentration of approximately $3 \times 10^{16}\text{ cm}^{-3}$, a resistivity of $0.11\text{ }\Omega\text{-cm}$, and a Hall hole mobility of $1820\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature. Vacuum firing minimized the primary contaminant, Na, and correspondingly lowered the carrier concentration to $4 \times 10^{14}\text{ cm}^{-3}$.

Introduction

Efficient thin-film heteroface $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ solar cells are of potential interest for use in large space arrays primarily because of their projected high specific power (1 kW/kg) and because of their superior radiation resistance (refs. 1 to 3). A promising approach to developing such thin-film cells is to epitaxially grow GaAs by vapor deposition techniques onto thin-film freestanding substrates. These films can also serve as the back contact on a Schottky barrier or junction device. The major consideration for the substrate is whether GaAs vapor deposited on the substrate will grow epitaxially and yield nominal electronic properties. Germanium appears to be a good substrate candidate, since the growth of high-efficiency thin-film GaAs shallow homojunction and heteroface photovoltaic cells using Ge and Ge-coated Si substrates has already been demonstrated (refs. 4 to 6). Further, Ge has very similar crystallographic characteristics to GaAs (e.g., diamond cubic crystal structure with approximately the same thermal coefficient of expansion) and is amenable to the heteroepitaxial growth of GaAs. The purpose of this paper is to report the growth of high quality, Ge thin-film ($\approx 10\text{ }\mu\text{m}$) single crystals that can be separated from a sacrificial NaCl substrate. These films were grown by plasma-enhanced chemical vapor deposition (PECVD) and their electronic properties are characterized.

Symbols and Abbreviations

E Auger electron energy

FWHM full width at half maximum, deg

I_{23}	sodium signal intensity
m/e	mass-to-charge ratio
$N(E)$	number of Auger electrons as a function of energy
PECVD	plasma-enhanced chemical vapor deposition
p	pressure, torr
rf	radio frequency
SIMS	secondary ion mass spectroscopy
TEM	transmission electron microscope
θ	Bragg diffraction angle, deg

Experiment

The technique utilized to grow separable thin-film Ge substrates required vapor deposition of Ge by PECVD onto polished NaCl(100) single crystals at 450°C . The Ge layers were then separated by either melting away the NaCl (raising the temperature to greater than 810°C) or by differential shear-stress techniques as the temperature was lowered. Physical vapor deposition methods and a similar PECVD method have been used previously by others (refs. 7 and 8) with limited success. The PECVD technique employed here involves the use of a radio frequency (rf) plasma generated above the NaCl substrate to break down the GeH_4 molecule. This method increases the energy of the free Ge atoms in excess of that obtained by normal thermal dissociation, thus improving the probability of epitaxial nucleation and growth. Epitaxial growth of Ge by PECVD occurs at substantially lower substrate temperatures than required when using ordinary chemical vapor deposition. (See ref. 9.)

The (100)NaCl crystals were polished under very light pressure for 20 minutes with a felt polishing pad that was continually flooded with a solution of HCl (70 percent by volume) and deionized H_2O (30 percent). The surface of the salt is shown in figure 1 at a magnification of 20000X and shows some defects, but overall the surface is essentially featureless. Immediately after drying in dry nitrogen, the salt was placed in the susceptor cavity of the PECVD reactor tube to minimize the adsorption of moisture and organic molecules. Susceptor is defined as an insert in the rf coil which provides efficient heating.

The reaction chamber was a fused-silica tube containing a cylindrical susceptor with an axial channel of rectangular cross section. (See fig. 2.) The base of the axial channel contains a square recessed volume in which the NaCl substrate was placed. In this

position, the substrate surface was either flush or below the base of the rectangular channel. A calibrated thermocouple for Ni10Cr-Ni3Mn2Al1Si was located in the immediate vicinity of the substrate. The susceptor was heated by rf at a frequency of 1.0 MHz, and a second rf coil (operating at an rf frequency of 13.56 MHz and located adjacent to and upstream of the carbon susceptor) was used to strike the plasma.

Procedure

The reactor tube was initially evacuated to 10^{-8} torr by ion pumping to insure that contamination from background gases was minimized. After the ion pump was valved off, high purity H_2 carrier gas was inlet at a flow rate of 190 cc/min and pumped by a double-trapped mechanical pump. The susceptor and the NaCl substrate temperature were then elevated to 450°C . After a short degassing period, 10-cc/min GeH_4 was added to the H_2 flow, and the rf plasma was initiated. The pressure in the reactor tube was then set at 0.75 torr for a 200-cc/min flow rate by adjusting the system pumping speed. Figure 3 shows the intensity of the 410.1-nm line of the hydrogen emission spectra as a function of input power. The hydrogen emission line was monitored with a photomultiplier tube and an interference filter. There are two thresholds which occur for this geometry: 10 W at plasma extinction and 17 W at plasma strike. Experiments conducted at 450°C with input power below the 10-W threshold showed no detectable Ge deposit on the NaCl. Since surface defects on the NaCl substrate surface generated by the sputtering and erosion of the plasma prior to nucleation are critical to the subsequent nucleation and ultimate quality of growth of the Ge, the power was immediately lowered to the minimum 10-W threshold after initiation of the plasma. At the onset of the plasma, Ge began to immediately deposit onto the NaCl surface. After several seconds, the desired nucleation was complete and the rf power was increased to 65 W to provide a higher growth rate ($\approx 10 \mu\text{m/h}$). No apparent degradation in the Ge crystallinity was observed for 65-W plasma power, presumably because nucleation was complete before the power increase, and the ordered first layers of Ge were quite stable, even with the increased power. Epitaxial growth of the Ge on NaCl using PECVD was quite sensitive to many other factors, such as substrate temperature, Ge deposition rate, GeH_4 flow rate and flow dynamics, substrate surface roughness, and surface contamination. The combined effect of these parameters is shown in figure 4. In part (a) of figure 4, a highly faceted but preferred orientation is obtained, whereas a more progressively ordered structure is obtained in parts (b) and (c) of

figure 4. In part (d) of figure 4, a highly ordered epitaxial Ge(100) growth has been achieved. The growth of the Ge nuclei seemed to follow the classic Volmer-Weber island growth, where oriented islands ultimately coalesced into a uniform film (ref. 9). The 450°C substrate temperature and the long growth times permitted some annealing of the growth defects. Another nonnegligible consideration is the NaCl vaporization rate. Ewing and Stern (ref. 10) have determined the rate of vaporization for the (100) face of NaCl with dislocation densities in the range of 2 to $5 \times 10^5 \text{ cm}^{-2}$. Using their data, the Na and Cl_2 flux leaving the surface at 450°C is $3 \times 10^{14} \text{ molecules-cm}^{-2}\text{s}^{-1}$. Therefore, in approximately 3 seconds, a monolayer is desorbed. At this rate, a sufficient number of surface defects can be generated in minutes to substantially alter the nucleation behavior. Experiments have shown that this may in fact be true, since the quality of the Ge films deteriorated with higher substrate temperatures. Furthermore, the Na content in the Ge was higher with increased substrate temperatures. It was, therefore, necessary to minimize the time the NaCl was at 450°C before GeH_4 was inlet and to minimize the initial plasma energy and time of exposure. These improvements over past methods of growing Ge thin films appear to be essential in achieving low-defect-density, high-quality material that is characteristic of ideal epitaxial growth.

Results and Discussion

After the desired film thickness was achieved, the temperature was lowered to 255°C (just above the transition of the NaCl from ductile to brittle) for several minutes to allow the strain in the interface caused by the difference in thermal coefficient of expansion ($\alpha_{Ge} = 6.2 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{NaCl} = 5 \times 10^{-5} \text{ K}^{-1}$) to be taken up by the still-ductile NaCl. Upon cooling to room temperature, the resulting shear at the interface routinely provided freestanding Ge films in excess of 1 cm^2 of surface area. In some cases, films as large as 6 cm^2 have been achieved, although they were normally achieved by melting away the NaCl substrate. The films were visually quite specular on both the interface and growth sides. Figures 5(a) and 5(b) show electron micrographs of a typical growth surface topography and the cleaved film edge for an $11\text{-}\mu\text{m}$ Ge film. Although the films were somewhat brittle, partly because of residual stresses from the lattice-parameter a_0 mismatch (Ge $a_0 = 5.658\text{\AA}$; NaCl $a_0 = 5.639\text{\AA}$ or 0.34 percent) and the separation, they were quite handleable with some care. The growth face still shows some surface structure, but significant annealing probably occurs during the growth interval ($t > 1 \text{ h}$), since the growth temperature is 60 percent of the Ge melting temper-

ature (1210 K). Figure 6 shows a sharp TEM (100) diffraction pattern for the films and a clean X-ray diffraction scan. The only X-ray diffraction peaks ($\text{Cu K}\alpha_1$, $\text{Cu K}\alpha_2$) were for the (400) orientation. A small (400) peak from residual $\text{Cu K}\beta$ is also shown. The intensity of the (400) doublet was quite large and was compared with the (400) doublet of a high-quality thick Ge single crystal. (See fig. 7.) Utilizing a 0.02° detection slit, the values of the full width at half maximum (FWHM) $\text{K}\alpha_1$ peak were found to be 0.07° and 0.056° , respectively. These values indicate a thin film of good quality. Examination of the surface contamination of the as-grown films by Auger electron spectroscopy (AES) showed the usual oxygen and carbon from exposure to air, but after Ar sputtering of less than 2.5 monolayers, a clean Ge spectrum was obtained. No other detectable contaminants were observed on the interface or growth side of the film (the sensitivity of the AES was ≈ 0.1 atomic percent). Energy dispersive analysis of X-rays (EDAX) emitted from the samples when examined by scanning electron microscopy (SEM) also indicated no detectable contamination (the sensitivity of the EDAX was ≈ 0.1 atomic percent). These spectra are shown in figures 8(a) and 8(b).

The Ge films were found to be p-type with a carrier concentration of $\approx 3 \times 10^{16} \text{ cm}^{-3}$. The room-temperature resistivity and Hall hole mobility were determined to be $0.11 \Omega\text{-cm}$ and $1820 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively, with corresponding values at 77.4 K of $0.05 \Omega\text{-cm}$ and $3300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The values compare favorably with the properties of bulk Ge single crystals. As previously indicated (ref. 11), the carrier concentration was thought to be a result of the free Na available from sublimation of the NaCl substrate at 450°C becoming incorporated into the lattice substitutionally and acting as an acceptor. As-grown films were examined by neutron activation analysis (NAA) and were found to contain 29 ppm Na. These films were subsequently vacuum fired at 800°C for 18 hours at a pressure of approximately 1×10^{-9} torr and were then reexamined by NAA. The Na content was reduced by an order of magnitude to ≈ 3 ppm which resulted in a carrier concentration of $\approx 4 \times 10^{14} \text{ cm}^{-3}$. This value is considerably lower than for the as-grown films, and it corresponds (ref. 12) to a room-temperature resistivity of $7 \Omega\text{-cm}$ and a Hall hole mobility of $2080 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Supporting experiments were also conducted with as-grown and vacuum-fired Ge films using secondary ion mass spectroscopy (SIMS). Although no quantitative measurements were made, the ratio of peak heights for the two cases is shown in figure 9 and was greater than 180. Figure 9 shows a substantial reduction of Na content and a consistency with the reduction in

carrier concentration and the concentration shown by the NAA data. Since the SIMS data were taken from the two contrasting Ge samples almost simultaneously (the two samples were mounted side by side on the same sample holder in the SIMS analysis chamber so they could be alternately examined within a few seconds under exactly the same conditions), they may actually be more indicative than the NAA data (3 ppm is near the detectability limit of the NAA instrument). Germanium films grown by ordinary CVD at 600°C on Si(100) substrates have also been reported and found to be p-type. (See refs. 13 and 14.) The carrier concentrations for these films were 10^{18} cm^{-3} with corresponding smaller hole mobilities and resistivities of $400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $10^{-2} \Omega\text{-cm}$, respectively. This difference in Ge quality could be the result of the higher diffusivity and solubility to contaminants at the growth temperature of 600°C .

Concluding Remarks

The method of plasma-enhanced chemical vapor deposition to grow high-quality Germanium thin-film crystals at its present state of refinement has been found to be quite successful, but many specific areas of the method can be further improved. For example, the plasma power threshold used herein was 10 W, but a modification of the geometry could reduce this level to less than 1 W, which would permit even finer control of the kinetics. Since the initial nucleation and growth ultimately controls the film defect density, the order of the resulting film might be significantly improved by substantially lowering the density of nuclei (growth appears to occur by the Volmer-Weber mechanism). This may also allow further reduction of the growth temperature, which in turn minimizes the adsorption and incorporation of contaminants. Another consideration is the continuum flow dynamics through the susceptor. The present geometry utilizes a NaCl substrate that is 100 percent of the width of the rectangular channel. Because of the corner effects, the flow over the middle of the substrate is considerably different than over the edges, which accounts for the ordered growth in the center of the substrate as compared with the faceted growth on the edges. A better arrangement would be to have the NaCl substrate much smaller than the channel width. Complete parametric studies were not conducted, but the ordered growth appeared to be most sensitive to the aforementioned parameters.

Acknowledgment

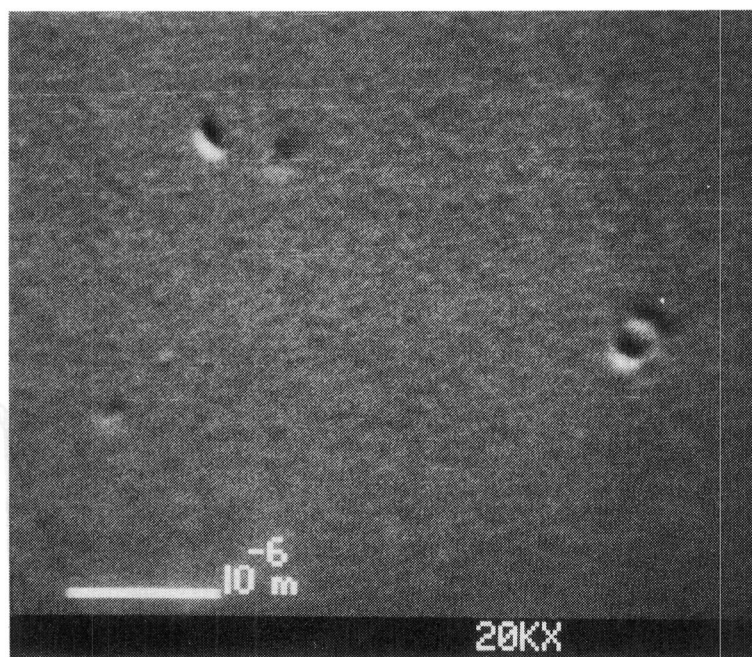
The authors gratefully appreciate the contributions of R. K. Crouch, G. H. Walker, and E. W.

Covington of Langley Research Center, W. A. Jesser of the University of Virginia, and R. Simchick of Kentron International.

NASA Langley Research Center
Hampton, VA 23665-5225
November 1, 1985

References

1. Randolph, Lynwood P.: Photovoltaic Outlook From the NASA Viewpoint. *Fifteenth IEEE Photovoltaic Specialists Conference—1981*, 81CH1644-4, pp. 10-13.
2. Kamath, G. S.: Recent Developments in GaAs Solar Cells. *18th Intersociety Energy Conversion Engineering Conference—"Energy for the Marketplace," Volume 3—Electrical Power Systems*, American Inst. Chem. Eng., c.1983, pp. 1224-1228.
3. Loo, R.; Knechtli, R. C.; and Kamath, G. S.: Enhanced Annealing of GaAs Solar Cell Radiation Damage. *Fifteenth IEEE Photovoltaic Specialists Conference—1981*, pp. 33-37.
4. Fan, John C. C.; Bozler, Carl O.; and Palm, Barbara J.: Calculated and Measured Efficiencies of Thin-Film Shallow-Homojunction GaAs Solar Cells on Ge Substrates. *Appl. Phys. Lett.*, vol. 35, no. 11, Dec. 1, 1979, pp. 875-878.
5. Stirn, R. J.; Wang, K. L.; and Yeh, Y. C. M.: Epitaxial Thin Film GaAs Solar Cells Using OM-CVD Techniques. *Fifteenth IEEE Photovoltaic Specialists Conference—1981*, 81CH1644-4, pp. 1045-1050.
6. Miller, D. L.; and Harris, J. S., Jr.: Molecular Beam Epitaxial GaAs Heteroface Solar Cell Grown on Ge. *Appl. Phys. Lett.*, vol. 37, no. 12, Dec. 15, 1980, pp. 1104-1106.
7. Skaggs, C. W.; and Jones, J. R.: Unsupported Single-Crystal Films of Germanium. *J. Appl. Phys.*, vol. 35, no. 10, Oct. 1964, pp. 3013-3015.
8. Shuskus, A. J.; and Cowher, M. E.: *Fabrication of Monocrystalline GaAs Solar Cells Utilizing NaCl Sacrificial Substrates*. R82-925171-30 (Subcontract No. XS-0-9002-5), United Technologies Research Center, 1982.
9. Vossen, John L.; and Kern, Werner, eds.: *Thin Film Processes*. Academic Press, Inc., 1978.
10. Ewing, Curtis T.; and Stern, Kurt H.: Vaporization Kinetics of Sodium Chloride. I. The Solid. *J. Phys. Chem.*, vol. 77, no. 11, May 24, 1973, pp. 1442-1449.
11. Outlaw, R. A.; and Hopson, P., Jr.: Free-Standing Thin Film Ge Single Crystals Grown by Plasma-Enhanced Chemical Vapor Deposition. *J. Appl. Phys.*, vol. 55, no. 6, Mar. 15, 1984, pp. 1461-1463.
12. Sze, S. M.: *Physics of Semiconductor Devices*, Second ed. John Wiley & Sons, Inc., c.1981, pp. 29-33.
13. Kuech, T. F.; Mäenpää, M.; and Lau, S. S.: Epitaxial Growth of Ge on 100 Si by a Simple Chemical Vapor Deposition Technique. *Appl. Phys. Lett.*, vol. 39, no. 3, Aug. 1, 1981, pp. 245-247.
14. Mäenpää, M.; Kuech, T. F.; Nicolet, M.-A.; Lau, S. S.; and Sadana, D. K.: The Heteroepitaxy of Ge on Si: A Comparison of Chemical Vapor and Vacuum Deposited Layers. *J. Appl. Phys.*, vol. 53, no. 2, Feb. 1982, pp. 1076-1083.



L-85-157

Figure 1. Surface topography of polished NaCl(100) substrate.

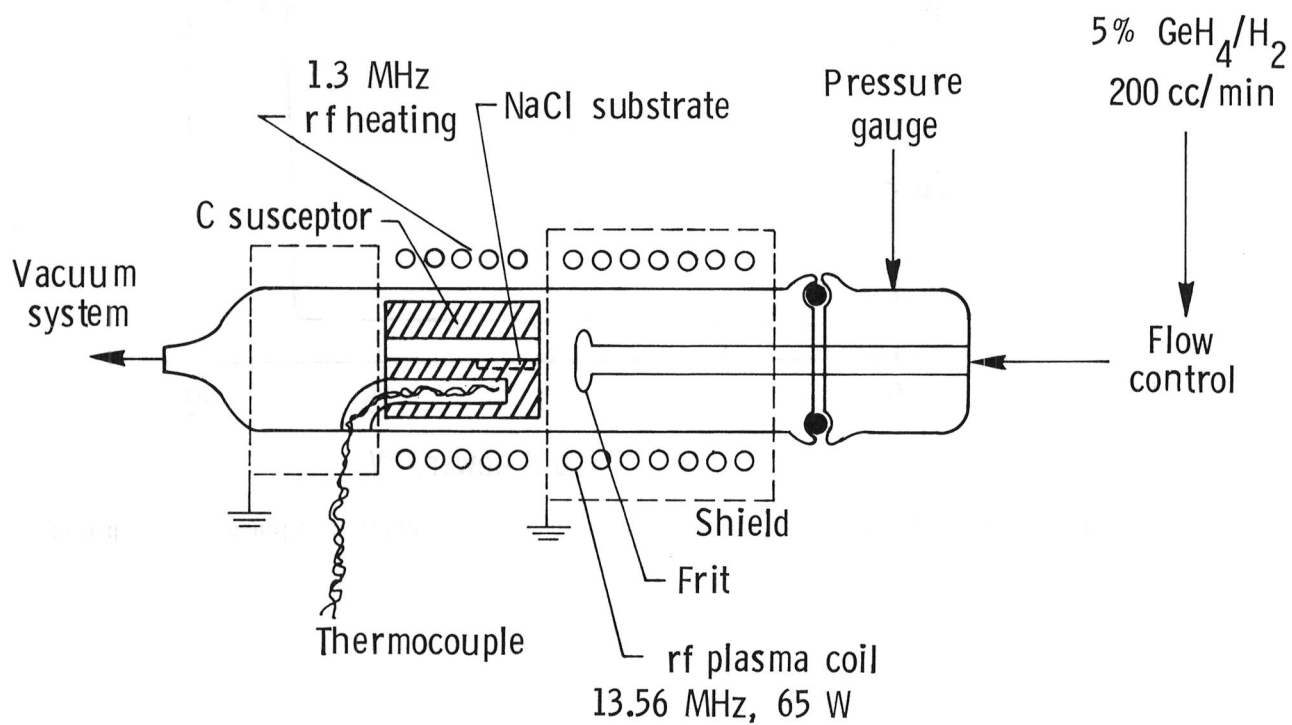


Figure 2. Fused-silica reactor tube.

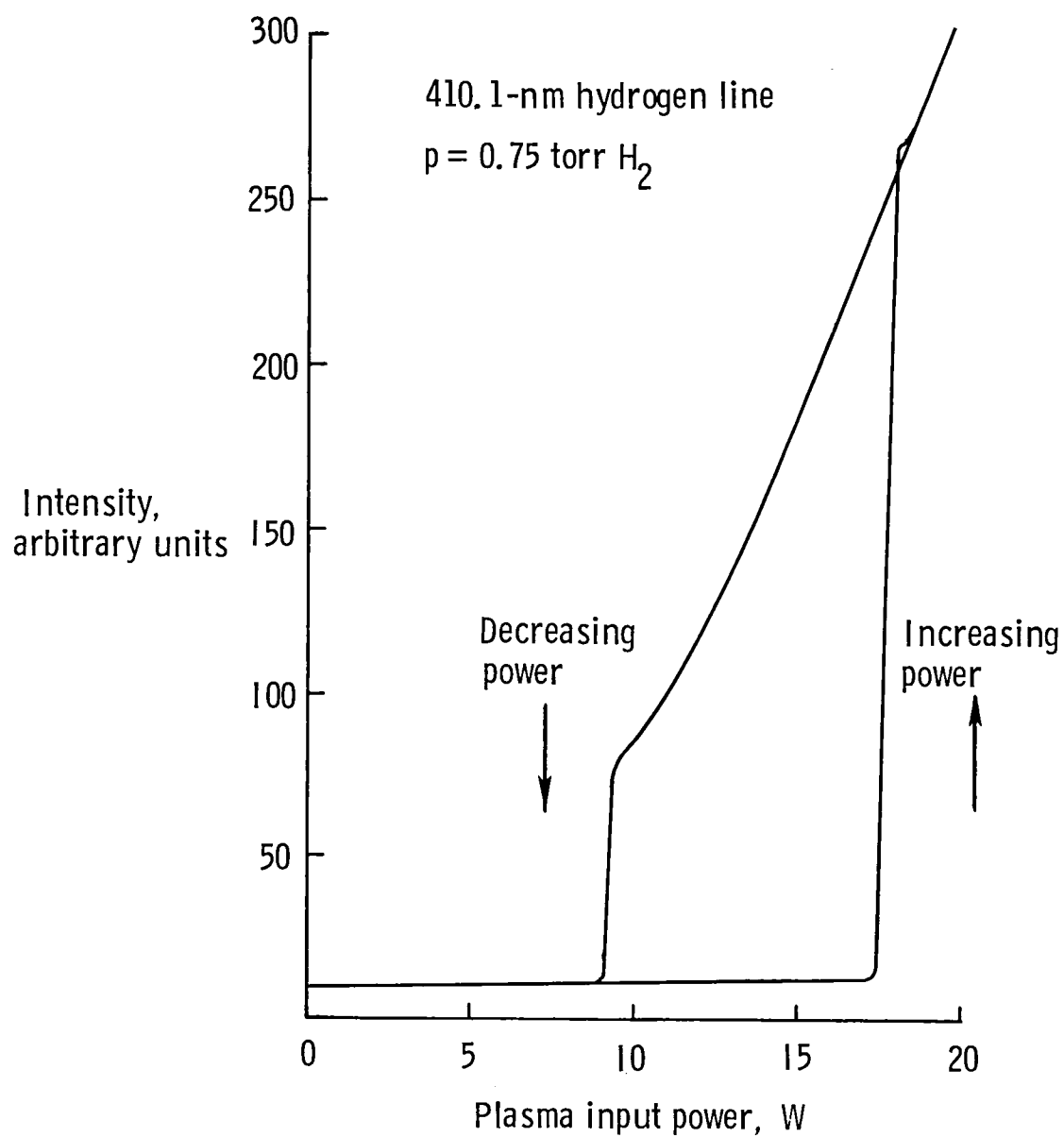
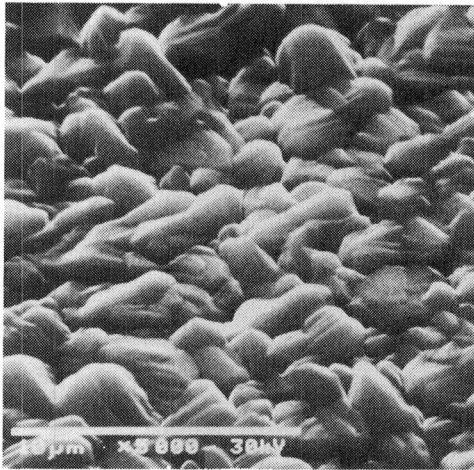
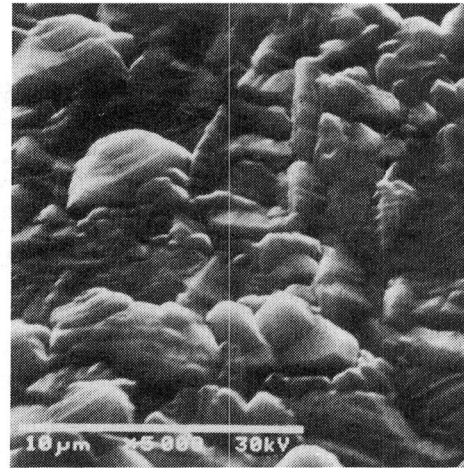


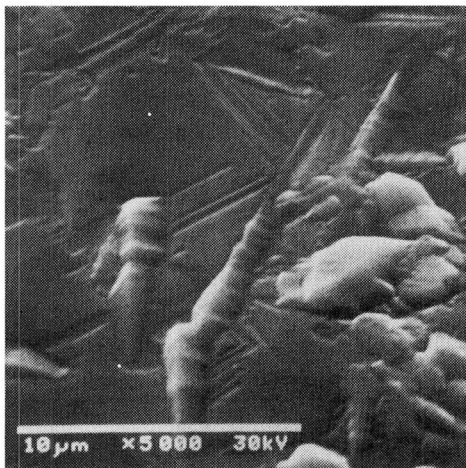
Figure 3. Intensity of hydrogen 410.1-nm spectral emission line as a function of plasma input power.



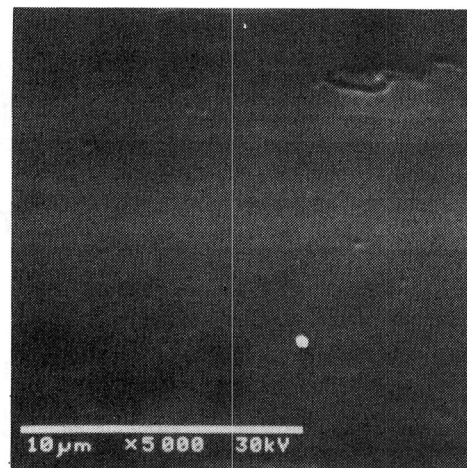
(a)



(b)



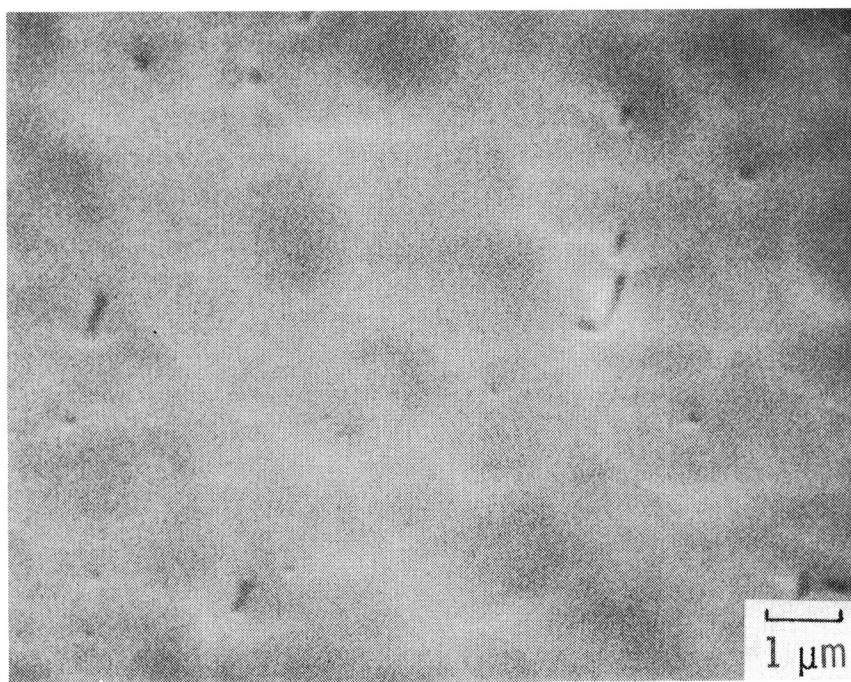
(c)



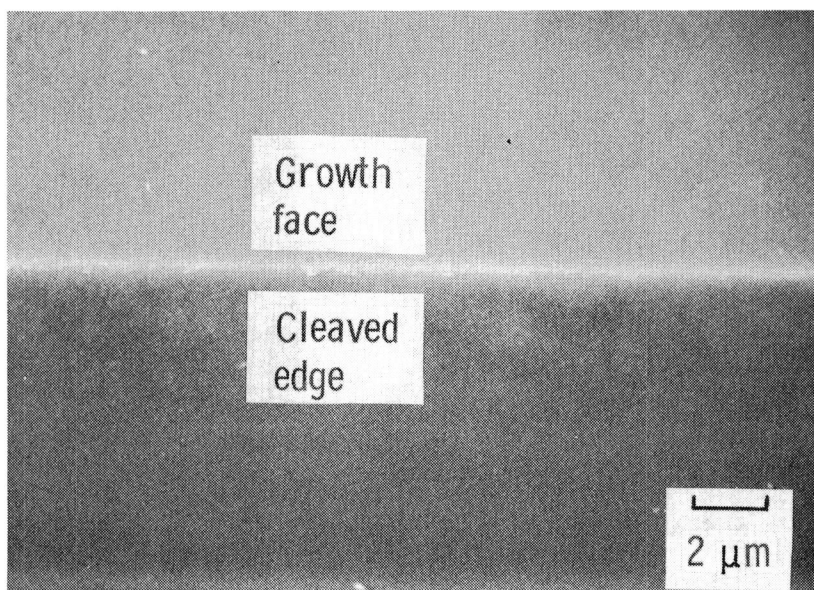
(d)

Figure 4. Various stages of complete epitaxy for Ge/NiCl(100).

L-85-158



(a) Surface topography of growth side.



(b) Film-edge cleavage.

L-85-159

Figure 5. Scanning electron micrographs of 11- μm Ge thin film.

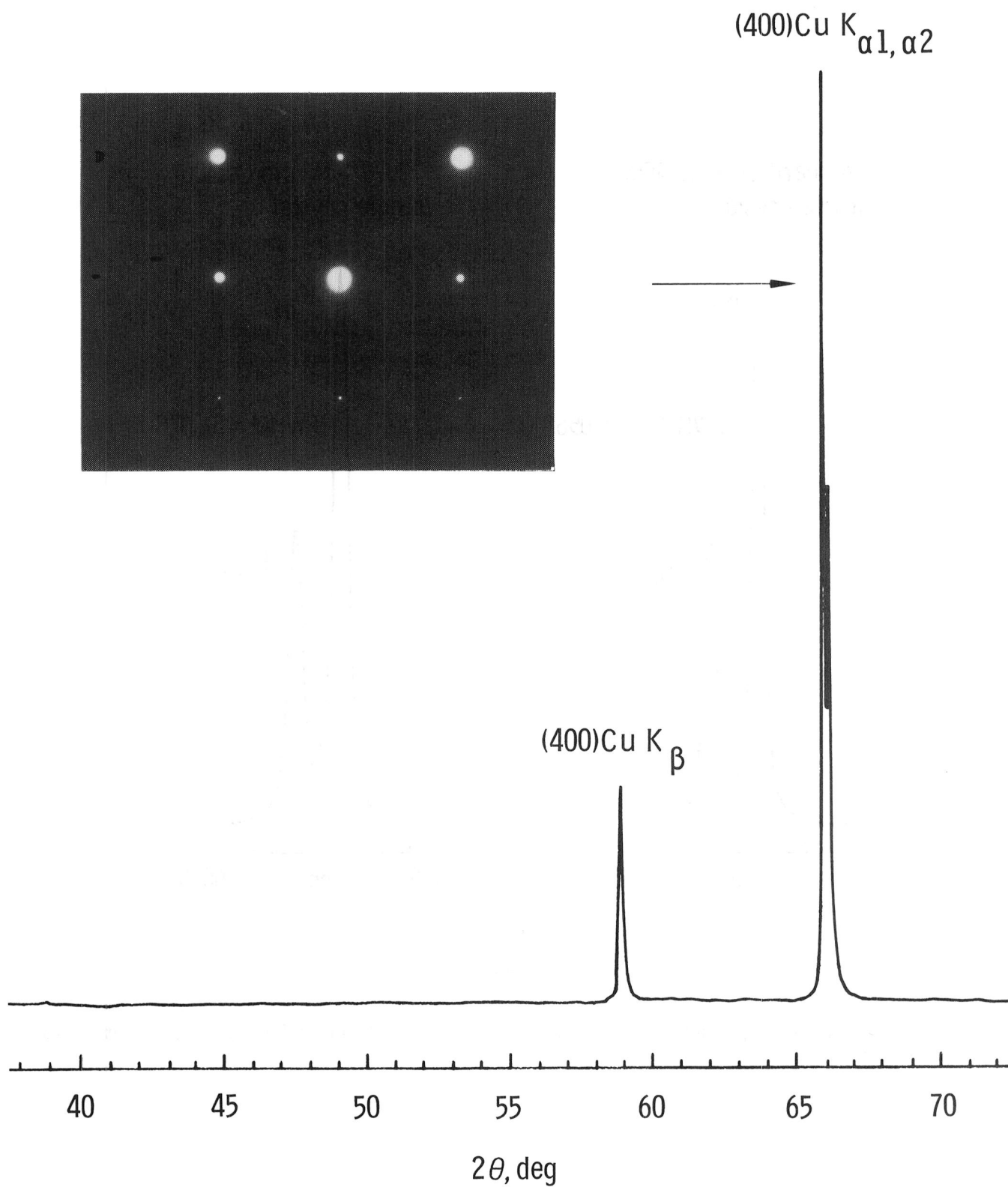
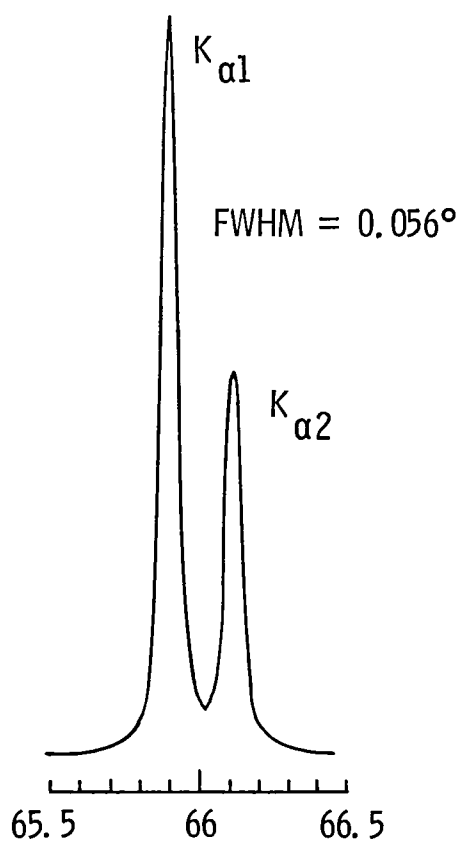
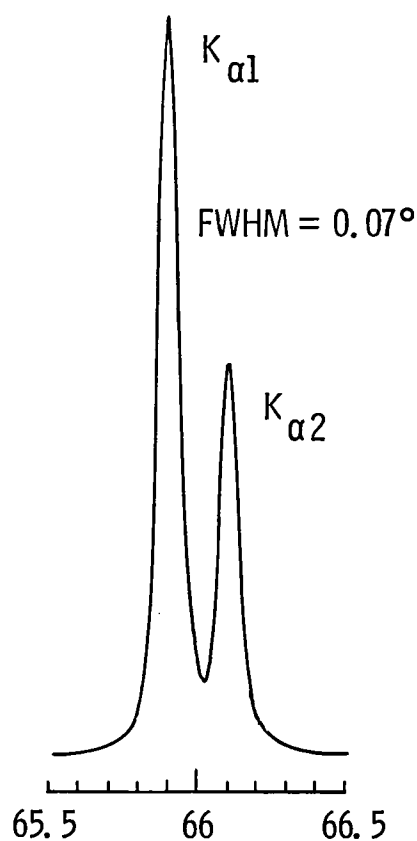


Figure 6. Sharp TEM diffraction pattern for Ge(100) orientation and X-ray diffraction scan of freestanding 11- μm Ge film.

Standard bulk Ge(400)
single crystal

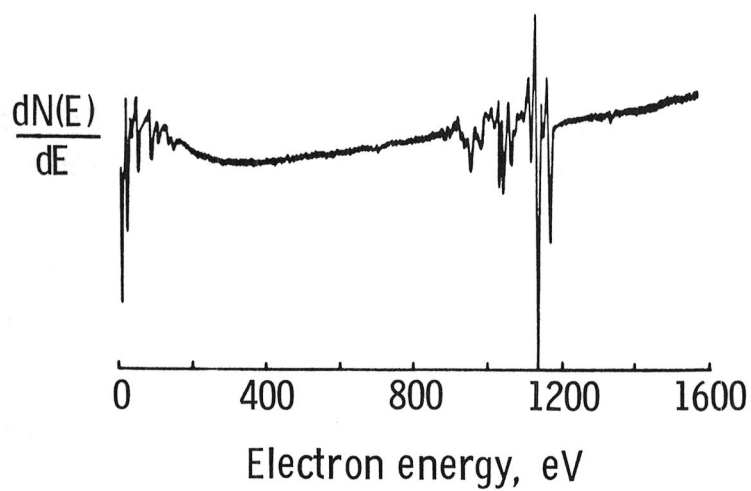


PECVD 11- μ m Ge(400)
single crystal

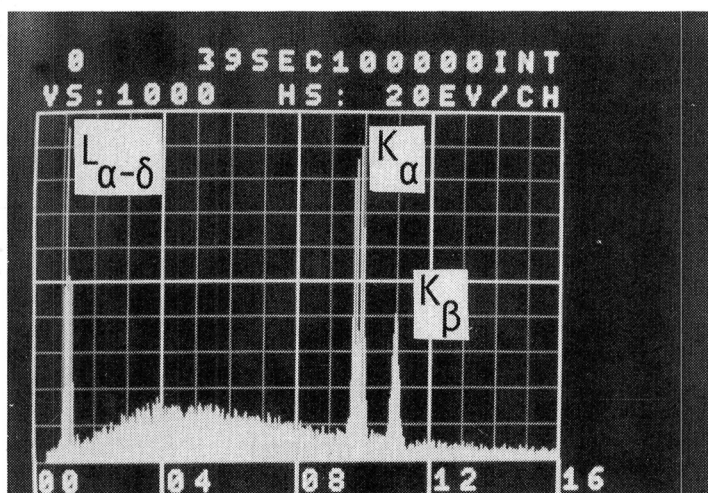


2θ , deg

Figure 7. Comparable Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ doublet structures for 11- μ m Ge film and high-quality thick Ge single crystal.

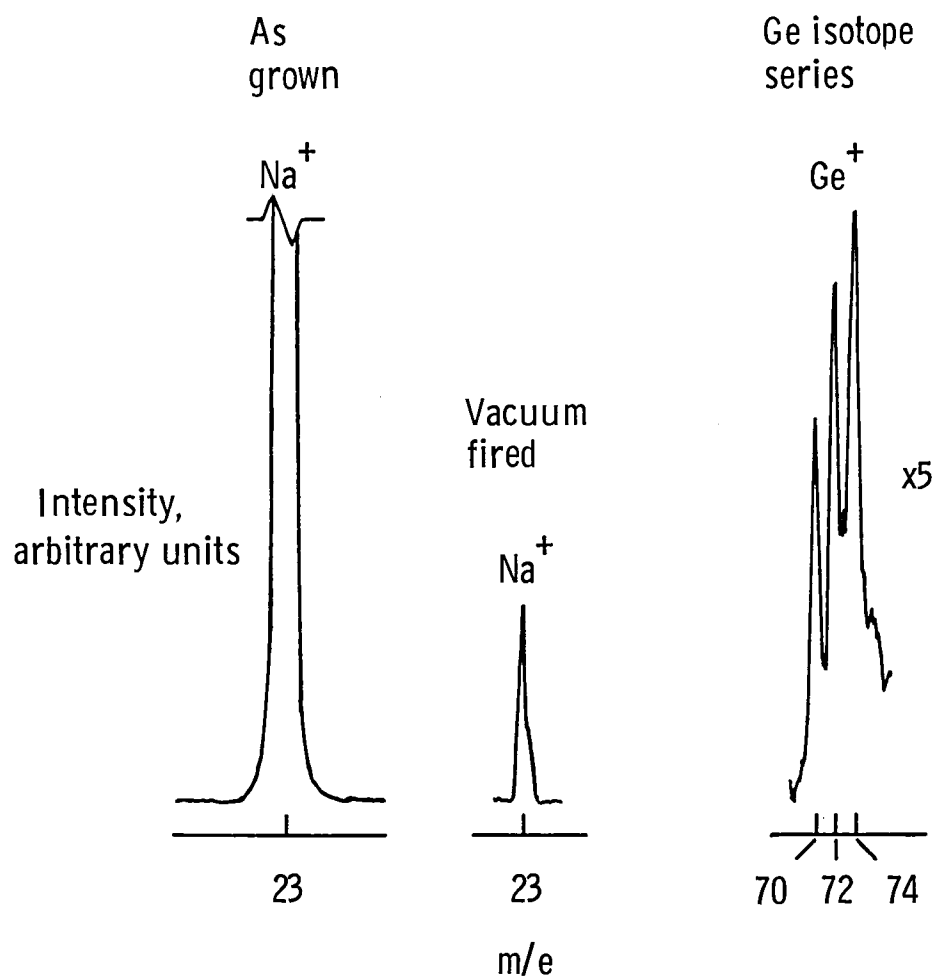


(a) Auger electron spectroscopy.



(b) Energy-dispersive analysis of X-rays.

Figure 8. Contamination analysis of Ge thin films.



$$\frac{I_{23}(\text{as grown})}{I_{23}(\text{vacuum fired})} = 180$$

Figure 9. SIMS spectra of Na signal in as-grown Ge compared with vacuum-fired Ge.

**National Aeronautics and
Space Administration
Code NIT-4**

**Washington, D.C.
20546-0001**

Official Business
Penalty for Private Use, \$300

**BULK RATE
POSTAGE & FEES PAID
NASA Washington, DC
Permit No. G-27**



**POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return**
